Postdepositional losses of methane sulfonate, nitrate, and chloride at the European Project for Ice Coring in Antarctica deep-drilling site in Dronning Maud Land, Antarctica

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[1] We quantified postdepositional losses of methane sulfonate (MSA\(^-\)), nitrate, and chloride at the European Project for Ice Coring in Antarctica (EPICA) drilling site in Dronning Maud Land (DML) (75\(^\circ\)S, 0\(^\circ\)E). Analyses of four intermediate deep firn cores and 13 snow pits were considered. We found that about 26 ± 13% of the once deposited nitrate and typically 51 ± 20% of MSA\(^-\) were lost, while for chloride, no significant depletion could be observed in firm older than one year. Assuming a first order exponential decay rate, the characteristic e-folding time for MSA\(^-\) is 6.4 ± 3 years and 19 ± 6 years for nitrate. It turns out that for nitrate and MSA\(^-\) the typical mean concentrations representative for the last 100 years were reached after 5.4 and 6.5 years, respectively, indicating that beneath a depth of around 1.2–1.4 m postdepositional losses can be neglected. In the area of investigation, only MSA\(^-\) concentrations and postdepositional losses showed a distinct dependence on snow accumulation rate. Consequently, MSA\(^-\) concentrations archived at this site should be significantly dependent on the variability of annual snow accumulation, and we recommend a corresponding correction. With a simple approach, we estimated the partial pressure of the free acids MSA, HNO\(_3\), and HCl on the basis of Henry’s law assuming that ionic impurities of the bulk ice matrix are localized in a quasi-brine layer (QBL). In contrast to measurements, this approach predicts a nearly complete loss of MSA\(^-\), NO\(_3\)\(^-\), and Cl\(^-\). INDEX TERMS: 0322 Atmospheric Composition and Structure: Constituent sources and sinks; 0330 Atmospheric Composition and Structure: Geochemical cycles; 0365 Atmospheric Composition and Structure: Troposphere—composition and chemistry; 1827 Hydrology: Glaciology (1863); 1863 Hydrology: Snow and ice (1827); KEYWORDS: postdepositional loss, snow chemistry, methane sulfonate


1. Introduction

[2] Polar ice cores represent an extraordinary archive of climate proxies from which information about temperature, precipitation, and composition of the paleo atmosphere can be derived in high temporal resolution [e.g., Legrand and Mayewski, 1997]. For example ionic impurities stored in the ice matrix are the result of atmospheric trace compound deposition and are potential proxies for the interaction between biogeochemical cycles and climate [e.g., Yang et al., 1997], as well as atmospheric circulation. Unfortunately, for certain ionic species, deposition seems to be reversible. For volatile acids HA (with A\(^-\) = formate, acetate, fluoride, chloride, nitrate, and methane sulfonate) postdepositional losses are partly well documented and described, especially for low accumulation sites in Antarctica and central Greenland [De Angelis and Legrand, 1995; Legrand et al., 1996; Wagnon et al., 1999; Röthlisberger et al., 2002, 2003; Delmas et al., 2003]. These previous investigations revealed that the mentioned acid species are not archived conservatively in the firm, complicating an interpretation of their profiles in ice cores. Concerning the physicochemical processes leading to postdepositional losses, there is some evidence that in acidic firm layers, the more or less volatile free acids HA are re-emitted to the firn air from which they are readily mixed within the atmospheric boundary layer by eddy diffusion [Wagnon et al., 1999]. Thus, as deduced by Wagnon et al. [1999] polar ice caps act as a source for once deposited volatile trace compounds, complicating not only the interpretation of their firm but also their atmospheric concentrations in polar regions. Mainly the strong and nonvolatile sulfuric acid, a dominant component in Antarctic snow and ice [Legrand and Mayewski, 1997] acts as potential H\(^+\) donor for the anions A\(^-\). In the special case of nitrate/HNO\(_3\), photolysis seems to be an additional and efficient loss mechanism within the upper firm layer [Dibb et al., 2002; Wolff et al., 2002] leading to significant NO\(_x\) emissions into the stable boundary layer above the snow.
surface [Honrath et al., 1999; Jones et al., 2001]. This mechanism is thought to have a dramatic impact on local photochemistry [Davis et al., 2001]. Previous investigations carried out in continental Antarctica revealed that loss of volatile acids is mainly restricted to the upper few meters in the firm [Wagnon et al., 1999], however, loss rates linked with this process have not yet been evaluated. In addition, while the influence of accumulation rate, firm acidity, and temperature on the firm concentrations of acid species has been described in several previous investigations [e.g., Legrand et al., 1996; Wagnon et al., 1999; Röthlisberger et al., 2002], quantification of total postdepositional losses are scarce [De Angelis and Legrand, 1995; Wagnon et al., 1999].

[1] In view of the present deep ice core drilling activities on Amundsenisen in the framework of the European Project for Ice Coring in Antarctica (EPICA), a characterization of postdepositional losses of the most prominent anions at the drilling site is obviously of basic importance. Accordingly, we focused our interest to provide a representative quantification of postdepositional losses and loss rates of methane sulfonate (MSA\textsuperscript{−}), nitrate (NO\textsubscript{3}\textsuperscript{−}), and chloride (Cl\textsuperscript{−}) in the upper firm layers at the EPICA drilling site in Dronning Maud Land (EDML). Furtheron, we try to assess the dependence of the observed losses on snow accumulation rate and address the question to what extentionic concentration profiles archived in the EDML ice core are influenced by the varying annual snow accumulation. To meet this aim, analyses of four intermediate deep ice cores and 13 snow pits were considered. Finally we will speculate about the physicochemical processes which may be responsible for the observed findings.

2. Site Selection, Sampling, and Analyses

[4] In the framework of EPICA, several comprehensive pre-site surveys have been carried out on Amundsenisen [Oerter et al., 1999, 2000]. Data from 13 snow pits and 4 intermediate-depth firm cores recovered during the field campaigns 1997/1998 and 1999/2000 are presented here (Figure 1). All drill sites are located in the Atlantic sector of the East Antarctic plateau more than 500 km away from the coast at an altitude range between 2600 and 3160 m above sea level (a.s.l.), i.e., well above the marine boundary layer. The mean annual snow accumulation (about 50–100 kg m\textsuperscript{−2} yr\textsuperscript{−1}) is rather low but varies by a factor of two between individual sites. Details on the location, altitude, dating of the cores and snow pits as well as sampling procedure and analysis can be found in the work of Göktaş [2002] and Göktaş et al. [2002]. In general, samples were analyzed for MSA\textsuperscript{−}, Cl\textsuperscript{−}, NO\textsubscript{3}\textsuperscript{−}, SO\textsubscript{4}\textsuperscript{2−}, Na\textsuperscript{+}, NH\textsubscript{4}\textsuperscript{+}, K\textsuperscript{+}, Mg\textsuperscript{2+}, and Ca\textsuperscript{2+} by ion chromatographic (IC) analysis. In short, the uncertainty for the measured ionic concentrations discussed in this study was approximately 3–5\% for the main components MSA\textsuperscript{−}, Cl\textsuperscript{−}, NO\textsubscript{3}\textsuperscript{−}, SO\textsubscript{4}\textsuperscript{2−}, Na\textsuperscript{+}, increasing to between 10\% and 20\% for the minor species NH\textsubscript{4}\textsuperscript{+}, K\textsuperscript{+}, Mg\textsuperscript{2+}, and Ca\textsuperscript{2+}.

3. Results

[5] Measured MSA\textsuperscript{−} and NO\textsubscript{3}\textsuperscript{−} concentrations vs. depth profiles for this region are presented in Figure 2. Surprisingly, none of the snow pits showed a significant Cl\textsuperscript{−} loss (Figure 3). Moreover, even for the Cl/Na ratio, which is a measure for excess chloride (i.e., HCl), we could not ascertain a significant decrease, neither for the Cl/Na maxima, nor for the mean values (Figure 3). MSA\textsuperscript{−} and NO\textsubscript{3}\textsuperscript{−} loss rates 1/τ [yr\textsuperscript{−1}] were calculated assuming a first order exponential decay according to:

\[ [A^-]_t = [A^-]_0 \exp\{-\Delta t/\tau\}. \]

where [A\textsuperscript{−}]\textsubscript{t} and [A\textsuperscript{−}]\textsubscript{0} denote the annual mean concentrations in a firm layer corresponding to the year t, and within the top layer of the snow pit at the year t\textsubscript{0} = 1997, respectively, with Δt = t\textsubscript{0}− t. Table 1 summarizes the results from all 13 snow pits, while in Figure 4 and Figure 5a and 5b the mean values comprising all snow pits are presented. In summary (8) from 13 snow pits showed a distinct NO\textsubscript{3}\textsuperscript{−} (MSA\textsuperscript{−}) decay vs. depth. There is no obvious explanation for the lack of NO\textsubscript{3} or MSA\textsuperscript{−} loss in the other pits. Note, however, that in each snow pit at least either a NO\textsubscript{3} or MSA\textsuperscript{−} decay was observed (Table 1). Based on our results we recommend an e-folding time of 6.4 ± 3 years for MSA\textsuperscript{−} (τ\textsuperscript{2} = 0.69) and 19 ± 6 years for NO\textsubscript{3} (τ\textsuperscript{2} = 0.97) being representative for the area of investigation on Amundsenisen. The quoted uncertainties refer to Figure 5 and represent the variabily between years averaged over the whole region. No significant correlation of loss rates with snow accumulation rate could be derived.

[6] We quantified the total loss of MSA\textsuperscript{−}, NO\textsubscript{3}, and Cl\textsuperscript{−} by relating [A\textsuperscript{−}]\textsubscript{0} to the 100 years mean concentrations [A\textsuperscript{−}]\textsubscript{100} retrieved from the firm cores (Table 2; starting from 1970 AD back to 1870 AD to exclude postdepositional impacts within the upper firm layers). Within the latter
interval, long-term trends in the corresponding concentration profiles are not detectable. We emphasize that we did not use fresh snow or surface snow concentrations of $A^-/C_0$ as a reference point to calculate the total loss. These concentrations turned out to be highly variable [Piel, 2004] and would not provide a robust benchmark. Ideally, $[A^-]/C_0$ in a given snow pit has to be compared with the long term mean of a core taken at the same site. In our case, only four medium deep cores are available for such an analysis. Within the given (small) range of snow accumulation rate in the area of investigation (55–97 kg m$^{-2}$ yr$^{-1}$), the loss rates and the mean MSA$^-$, Cl$^-$, and NO$_3^-$ concentrations found in the snow pits exhibited no significant dependence on the snow accumulation rate ($r^2 < 0.1$ in all cases). In contrast, for $[A^-]_{100}$ a dependence on snow accumulation rate is observed (Figure 6 and Table 2). Here, MSA$^-$ and NO$_3^-$ concentrations in firm indicated less depositional losses at higher accumulation rates [Göktaş et al., 2002], while Cl$^-$ concentrations showed the reverse relation. The influence of the snow accumulation rate (accu) on MSA$^-$ concentrations can be quantified by the following expression:

$$[\text{MSA}^-] = (0.12 \times \text{accu} - 0.87) \text{ng g}^{-1} \quad r^2 = 0.98.$$  

For [NO$_3^-$] and [Cl$^-$] the linear regressions given in Figure 6 are not significant ($F$ test below a significance level of $\alpha = 0.1$).

[7] To simplify matters, we related $[A^-]_{100}$ of the cores to $[A^-]_{t0}$ of pits with comparable snow accumulation rates (accu): Core DML03 with pits DML13,14,19–21 (accu = 78–98 kg m$^{-2}$ yr$^{-1}$); core DML05 with pits

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Figure 2. Nitrate (solid line, left-hand scale) and MSA$^-$ (dashed line, right-hand scale) concentrations as a function of depth, measured in 12 snow pits (results from pit DML25/8 are shown in Figure 8.

Figure 3. Chloride concentration and Cl/Na ratio as a function of depth, measured in a snow pit excavated at the site DML19. The Cl/Na ratio for seawater is about 1.8. The horizontal broken line represents the corresponding 100 year mean ([Cl$^-]_{100}$) of the firm cores.
Table 1. Summary of the Results From 13 Snow Pits, Including Mean Snow Accumulation Rates and the Number of Years Covered by Each Snow Pit

<table>
<thead>
<tr>
<th>Snow Pit</th>
<th>Accumulation Rate, kg m⁻² yr⁻¹</th>
<th>Number of Years</th>
<th>MSA⁻, ng g⁻¹</th>
<th>Cl⁻, ng g⁻¹</th>
<th>NO₃⁻, ng g⁻¹</th>
<th>¹/₀MA⁻/₀/A⁻, yr⁻¹</th>
<th>¹/₀minexpo, yr⁻¹</th>
<th>Δ[MSA⁻]ᵣₒ totalitarian, ng g⁻¹</th>
<th>Δ[Cl⁻]ᵣₒ totalitarian, ng g⁻¹</th>
<th>Δ[NO₃⁻]ᵣₒ totalitarian, ng g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>DML25/1</td>
<td>72</td>
<td>9</td>
<td>9.8 (17.2)</td>
<td>45.9 (36.4)</td>
<td>59.2 (50.7)</td>
<td>0.08</td>
<td>(*)</td>
<td>-10.7</td>
<td>+9.7</td>
<td>-3.7</td>
</tr>
<tr>
<td>DML25/8</td>
<td>72</td>
<td>9</td>
<td>11.8 (20.5)</td>
<td>38.9 (35.3)</td>
<td>64.8 (56.0)</td>
<td>0.08</td>
<td>(*)</td>
<td>-14.0</td>
<td>+10.8</td>
<td>-9.0</td>
</tr>
<tr>
<td>DML18</td>
<td>55</td>
<td>10</td>
<td>9.1 (24.5)</td>
<td>57.3 (50.3)</td>
<td>59.2 (81.3)</td>
<td>0.24</td>
<td>0.076</td>
<td>-19.5</td>
<td>+8.4</td>
<td>-40.3</td>
</tr>
<tr>
<td>DML07</td>
<td>62</td>
<td>10</td>
<td>13.9 (27.5)</td>
<td>70.7 (84.5)</td>
<td>62.2 (77.0)</td>
<td>(*)</td>
<td>0.060</td>
<td>0.060</td>
<td></td>
<td></td>
</tr>
<tr>
<td>DML19</td>
<td>78</td>
<td>11</td>
<td>7.1 (16.4)</td>
<td>50.7 (36.9)</td>
<td>55.0 (69.5)</td>
<td>0.18</td>
<td>(*)</td>
<td>-6.6</td>
<td>+10.4</td>
<td>-15.5</td>
</tr>
<tr>
<td>DML05</td>
<td>71</td>
<td>10</td>
<td>10.6 (9.9)</td>
<td>47.6 (62.0)</td>
<td>56.6 (58.3)</td>
<td>(*)</td>
<td>0.022</td>
<td>-3.4</td>
<td>+15.9</td>
<td>-11.3</td>
</tr>
<tr>
<td>DML20</td>
<td>97</td>
<td>8</td>
<td>8.6 (11.8)</td>
<td>26.5 (37.8)</td>
<td>60.3 (73.1)</td>
<td>0.15</td>
<td>0.022</td>
<td>-2.0</td>
<td>+9.5</td>
<td>-19.1</td>
</tr>
<tr>
<td>DML21</td>
<td>83</td>
<td>9</td>
<td>14.1 (11.9)</td>
<td>37.6 (36.2)</td>
<td>85.8 (82.1)</td>
<td>(*)</td>
<td>0.088</td>
<td>-2.1</td>
<td>+11.1</td>
<td>-28.1</td>
</tr>
<tr>
<td>DML17</td>
<td>63</td>
<td>14</td>
<td>6.2 (16.2)</td>
<td>37.9 (50.3)</td>
<td>57.2 (72.2)</td>
<td>0.16</td>
<td>0.065</td>
<td>-10.5</td>
<td>+5.6</td>
<td>-19.2</td>
</tr>
<tr>
<td>DML15</td>
<td>71</td>
<td>8</td>
<td>13.0 (18.9)</td>
<td>33.4 (57.0)</td>
<td>60.9 (81.5)</td>
<td>(*)</td>
<td>0.089</td>
<td>-12.4</td>
<td>-10.9</td>
<td>-34.5</td>
</tr>
<tr>
<td>DML14</td>
<td>81</td>
<td>9</td>
<td>12.0 (18.6)</td>
<td>42.7 (34.7)</td>
<td>50.1 (79.4)</td>
<td>(*)</td>
<td>0.055</td>
<td>-8.8</td>
<td>+12.6</td>
<td>-25.4</td>
</tr>
<tr>
<td>DML13</td>
<td>80</td>
<td>10</td>
<td>9.4 (17.8)</td>
<td>48.6 (116)</td>
<td>55.1 (83.2)</td>
<td>0.24</td>
<td>0.099</td>
<td>-8.0</td>
<td>-68.7</td>
<td>-29.2</td>
</tr>
<tr>
<td>DML12</td>
<td>68</td>
<td>9</td>
<td>9.5 (11.7)</td>
<td>64.7 (77.5)</td>
<td>54.8 (47.1)</td>
<td>(*)</td>
<td>0.099</td>
<td>-5.2</td>
<td>-31.4</td>
<td>-0.1</td>
</tr>
</tbody>
</table>

*Mean concentrations of the ions are presented along with the annual mean values of the top layer, [A⁻]₀₀ (in parentheses); (*) indicates that no decay could be detected in the snow pit samples, while usually there is a loss Δ[A⁻]ᵣₒ totalitarian relative to the cores. For definition of first-order loss constants ¹/₀minexpo and the total loss Δ[A⁻]ᵣₒ totalitarian, see text. The accuracy of Δ[A⁻]ᵣₒ totalitarian is about ±(15–20)%.

Figure 4. Averages of the annual mean MSA⁻ (gray triangles; note different scale), Cl⁻ (diamonds), and NO₃⁻ (circles) concentrations from 13 snow pits as a function of firm age. The error bars indicate the standard deviations of the values.

Figure 5. Mean first-order exponential decay of MSA⁻ (a) and NO₃⁻ (b) derived from all 13 snow pits. Error bars represent the corresponding standard deviations (±std) of the annual mean values from the different snow pits.
[8] Again, considering all snow pits, a significant Cl\(^{-}\) or excess chloride loss could not be found (2 ± 33%), while in contrast about 26 ± 13% of the once deposited NO\(_3\) and 51 ± 20% of MSA\(^{-}\) were not preserved in firn. Only for MSA\(^{-}\) the quantified relative loss ΔMSA\(_{\text{rel}}\) [%] showed a distinct correlation with the snow accumulation rate (r\(^2\) = 0.69, Figure 7):

\[
\Delta \text{MSA}_{\text{rel}}[\%] = -(1.6 ± 0.3) \times \text{accu} + (168 ± 24)
\]

[r\(^2\) = 0.69, Equation (1)]

[9] Below a characteristic depth Δz of around 1.2 ± 0.2 m and 1.4 ± 0.2 m the mean MSA\(^{-}\) and NO\(_3\) concentrations, respectively, reached the 100 year mean concentrations of the cores. The threshold depth Δz was derived from the calculated mean first order loss rates and the observed mean total losses, assuming a firn density of 0.35 g cm\(^{-3}\) and calculated mean first order loss rates and the observed mean temperature T = 4.1oC (Oerter et al., 1999). Note that data presented by Delmas et al. [2003, Figure 2] from Vostok indicate that postdepositional losses of nitrate ceased beyond a depth of around 1.5 m, while for MSA the situation appears less clear.

4. Discussion

4.1. Comparison With Previous Results

From Antarctica

[10] The higher total postdepositional loss of MSA\(^{-}\) and NO\(_3\) observed at Vostok (78°28’S, 106°48’E, 3490 m a.s.l., annual mean temperature T = –56°C) and Dome C (74°39’S, 124°10’E, 3240 m a.s.l., T = –53.5°C) compared to our findings may be attributed to the much lower accumulation rate at these sites (Table 3). Röthlisberger et al. [2000] found a pronounced temperature dependence of nitrate concentrations archived at different Antarctic sites with higher concentrations at lower annual mean temperature. This tendency may partly compensate the impact of snow accumulation rate. However, Table 3 reveals that the latter factor is clearly dominant (note that annual mean temperature at EPICA DML is –46°C).

[11] The lack of a postdepositional Cl\(^{-}\) loss at DML05 remains peculiar. Although our fresh and surface snow samples taken from this site during austral summer showed high Cl/Na ratios between 6 and 12 [Piel, 2004], Cl/Na was around 2.3 ± 1 in the snow pits and firm cores, close to the sea salt ratio of 1.8. These fresh and surface snow samples further indicate that most of the excess chloride (HCl) and about 50% of nitrate, were typically lost within a few weeks [Piel, 2004]. In contrast MSA\(^{-}\) postdepositional depletion seemed to occur more gradually. In contrast, at Vostok the Cl/Na ratio decreased from a value of 5 in the upper 2 m to about 0.3–0.4 at greater depth [Wagnon et al., 1999]. Recently Röthlisberger et al. [2003] observed significant Cl\(^{-}\) deficits relative to Na\(^{+}\) below a threshold accumulation rate of about 40 kg m\(^{-2}\) yr\(^{-1}\) in EPICA Dome C ice core. Results from Wagnon et al. [1999] revealed a distinct positive correlation between Na\(^{+}\) and non sea salt sulfate concentrations, but not with Cl\(^{-}\), indicating that Na\(^{+}\) was associated with sulfate due to the reaction of sulfuric acid aerosol with NaCl. In contrast, our findings clearly showed the contrary relation, suggesting that deposited sea salt was persistent. These differences may be attributed to the different location and precipitation regime. While DML, which is about 500 km away from the coast, is subject to cyclonic activity and receives about 80% of its precipitation from frontal clouds [Reijmer et al., 2002], low accumulation

![Figure 6](image1)

**Figure 6.** Dependence of the MSA\(^{-}\) (triangles; note different scale), NO\(_3\) (circles), and Cl\(^{-}\) (diamonds) concentrations found in 4 firm cores (100 year means from 1970 to 1870 AD) on the snow accumulation rate. In contrast to the results from the snow pits in each case a significant correlation is given (m = slope [10\(^{-9}\) yr kg\(^{-1}\) m\(^{-2}\)], b = intercept [ng g\(^{-1}\)]).

![Figure 7](image2)

**Figure 7.** Dependence of the relative MSA\(^{-}\) (triangles) and NO\(_3\) (circles) losses on the snow accumulation rate (m = slope [yr kg\(^{-1}\) m\(^{-2}\)], b = intercept [%]).
sites like Vostok are extremely remote and diamond dust seems to be the primary way of precipitation. Accordingly, snow formation, hence wet deposition of aerosol, and subsequently recrystallization processes in the snowpack are expected to differ between the two regimes, leading to different aerosol deposition as well as preservation.

[12] Striking MSA$^-$/CO$_2$ peaks could be found in nearly all snow pits in 1997 and 1992 AD. These outstanding MSA$^-$/CO$_2$ concentration peaks could be retrieved in two snow pits excavated two years later close to this site (Figure 8). We conclude that in spite of distinct postdepositional MSA$^-$/CO$_2$ losses, the overall signature of MSA$^-$/CO$_2$ concentration profiles remained preserved. However, more subtle (tens of percent) changes in peak concentrations could still be masked by typical accumulation rate changes (Figure 8). To exclude a possible bias by the MSA$^-$/CO$_2$ concentration peak in 1996/1997 AD in calculating the first order loss rate, we re-evaluated $\tau_{\text{MSA}}$ considering only the years from 1995/1996 back to 1990/1989 AD. This results in a slightly, but negligibly lower e-folding time of 6.3 ± 3.5 years ($r^2 = 0.63)$. As mentioned by Göktaş et al. [2002], a migration of MSA$^-$ peaks away from highly acidic H$_2$SO$_4$ layers, evident in firm cores from other Antarctic sites [Minikin et al., 1994; Pasteur and Mulvaney, 2000; Curran et al., 2002; Delmas et al., 2003] could not be unequivocally verified, even in our high resolution snow pit samples (DML25/8, about 10 samples per year).

4.2. Possible Physicochemical Processes Causing HA Loss

[13] There are two potential physicochemical processes which are most probably responsible for the observed losses: Formation of volatile acids HA in acidic snow layers which are partially re-emitted to the atmosphere [Wagnon et al., 1999], or photochemical reactions of HA or A$^-$ within the firm layer. The latter process is known to act as a significant nitrate/HNO$_3$ loss mechanism [Dibb et al., 2002; Wolff et al., 2002]. Even for MSA photo-oxidation could be relevant: Milne et al. [1989] measured a rather fast reaction rate of MSA with OH radicals in aqueous solutions ($k_{398K} = 4.7 \pm 0.9 \times 10^7$ M$^{-1}$ s$^{-1}$) and estimated a typical lifetime of MSA in midlatitude cloud droplets of only 1.2–3.5 hours. Applied to our conditions, an average OH concentration in the quasi-brine layer (see below) of around 10$^{-16}$ M would be sufficient to cause the observed MSA decay rate in upper firm layer. However, as stated by Wolff et al. [2002] in case of postdepositional nitrate loss, below a depth of about 10 cm actinic radiation can be expected to become insignificant. Consequently a continuous loss of nitrate and MSA$^-$ down to a depth of 1.2–1.4 m cannot be attributed to photochemistry.

[14] In the following approach, which is mainly drawn upon the proceeding of Cho et al. [2002] we will assess whether formation of the volatile free acids is a potential Table 3. Summary of Reported Postdepositional Losses of MSA$^-$, NO$_3^-$, and Cl$^-$ Found in Snow Pits or Firn Cores Drilled at Vostok, Dome C, South Pole, and DML05 (This Work) With the Corresponding Snow Accumulation Rates in Parentheses

<table>
<thead>
<tr>
<th>Anion</th>
<th>Vostok, a</th>
<th>Dome C, b</th>
<th>South Pole, c</th>
<th>EPICA–DML, d</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSA$^-$</td>
<td>90%±4%</td>
<td>72%±7%</td>
<td>80%±4%</td>
<td>61±13%</td>
</tr>
<tr>
<td>NO$_3^-$</td>
<td>90%±4%</td>
<td>72%±7%</td>
<td>no trend e</td>
<td>30±15%</td>
</tr>
<tr>
<td>Cl$^-$</td>
<td>80%±4%</td>
<td>70%±4%</td>
<td>no trend b</td>
<td>5±32%</td>
</tr>
</tbody>
</table>

aFrom De Angelis and Legrand [1995].
bFrom Legrand and Delmas [1988].
cFrom Mayewski and Legrand [1990].
dFrom Wagnon et al. [1999].
eFrom Röthlisberger et al. [2000].
fFrom Röthlisberger et al. [2003].
Table 4. Molal Ionic Concentrations in Bulk Ice and Within the Quasi-Brine Layer (QBL), Ratios of the Free Acids HA in the QBL, Henry’s Law Constants for HA, Corresponding Equilibrium Mixing Ratios of Gaseous HA According to Henry’s Lawa

<table>
<thead>
<tr>
<th>Anion</th>
<th>Bulk Ice, µmol kg⁻¹</th>
<th>QBL, mol kg⁻¹</th>
<th>[HA][A⁻]m, mol L⁻¹ atm⁻¹</th>
<th>pHHA/p0 (Mixing Ratio)</th>
<th>Atmospheric Mixing Ratio of HA</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSA⁻</td>
<td>0.095</td>
<td>0.26</td>
<td>0.83</td>
<td>8.97 x 10¹¹</td>
<td>0.36 x 10⁻¹²</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>0.83</td>
<td>2.3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>NO₃⁻</td>
<td>0.79</td>
<td>2.2</td>
<td>0.34</td>
<td>1.55 x 10⁸</td>
<td>7.3 x 10⁻⁹</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>1.04</td>
<td>2.9</td>
<td>2.4 x 10⁻⁴</td>
<td>30</td>
<td>3.5 x 10⁻⁶</td>
</tr>
<tr>
<td>H⁺</td>
<td>2.27</td>
<td>6.4</td>
<td>-</td>
<td>-</td>
<td>80 x 10⁻¹²</td>
</tr>
</tbody>
</table>

*Here p₀ = 680 hPa, i.e., the air pressure at the sampling site, and typical atmospheric HA mixing ratios are presented. For details, see text.

[a] From Mauldin et al. [2001].
[b] From Weller et al. [2002].
[c] From Piel [2004].

process to explain the observed postdepositional losses. Recent investigations suggest that during snow metamorphism, organic impurities are excluded from ice crystals and concentrated in a quasi-brine layer, QBL [Conklin and Bales, 1993; Cho et al., 2002]. Hence we assumed that all organic impurities are accumulated within the QBL. According to Cho et al. [2002] the needed total electrolyte concentration within the QBL to enable a melting point depression ΔT of ~30 K, which is typical for summer snow layers in the area of investigation, was estimated by the expression:

\[
\text{ln} x_{H,O} = - \frac{\Delta H_{ice}}{RT_m} \left( \frac{T_m - T}{T} \right)
\]

The variables are defined as follows: \(x_{H,O}\), mole fraction of H₂O; \(\Delta H_{ice}\), the melting enthalpy and \(T_m\), melting point of pure ice. We obtained an enrichment of the ionic concentrations (with \(\Sigma x = 1 - x_{H,O}\)) in the QBL by a factor of \(2.8 \times 10^9\) compared to the bulk ice (Table 4). Assuming that an ice grain with a diameter of 200 µm is covered by the calculated amount of quasi-brine, the thickness of this layer would be about 0.1 Å, much less than a molecular monolayer and consequently unrealistic. This indicates that either individual droplets of QBL are distributed inhomogeneously across the crystal surface, or more probably, localized at grain boundaries and triple junctions [Fukazawa et al., 1998; Barnes et al., 2003].

To estimate the equilibrium concentrations of the free acids HA we calculated the concentration of H⁺ from the measured ion balance assuming that the difference between the anion and the cation equivalents corresponds roughly to the H⁺ equivalents (\([\text{ion}]_e\) is given in µeq g⁻¹):

\[
[\text{H}^+]_e = [\text{MSA}^-]_e + [\text{Cl}^-]_e + [\text{NO}_3^-]_e + [\text{SO}_4^{2-}]_e - [\text{Na}^+]_e - [\text{NH}_4^+]_e - [\text{K}^+]_e - [\text{Mg}^{2+}]_e - [\text{Ca}^{2+}]_e
\]

The ion balance determined from our snow pit samples led to the result that 82 ± 7% of the cation equivalents are H⁺. Accordingly, the molal concentrations (moles of solute per 1000 g of solvent [mol kg⁻¹]) of the free acids [HA]ₐ (\(A^- = \text{MSA}^-\), NO₃⁻, and Cl⁻) were determined by the expression:

\[
K_a = \frac{\gamma(H^+)_{m}[A^-]_{m}}{[HA]_{m}}
\]

where \(K_a\) denotes the acidity constant of HA, \(\gamma\) ± is the corresponding activity coefficient, taken from Hamer and Wu [1972] in case of HNO₃ and HCl. For MSA we took the value given by Covington et al. [1973]; \([A^-]_{m} = [A^-]_{m,total} - [HA]_{m}\); \(pK_a(\text{MSA}) = -1.84\), \(pK_a(\text{HNO}_3) = -1.4\), \(pK_a(\text{HCl}) = -7.0\). The equilibrium partial pressure of gaseous HA can be derived from Henry’s law:

\[
H_{HA} \times [HA]_{m} = p_{HA}
\]

where \(H_{HA}\) is Henry’s law constant for HA at 243 K, taken from Schwartz and White [1981], Dean [1992], and from Clegg and Brimblecombe [1985] for HNO₃, HCl, and MSA (only available at \(T = 298\) K, respectively; \(p_{HA}\) is equilibrium partial pressure of HA. The final results of these calculations are summarized in Table 4.

[16] Very clearly, assuming thermodynamic equilibrium conditions with the corresponding atmospheric mixing ratios the volatile acids MSA, HNO₃ and HCl should be re-emitted nearly quantitatively (Table 4). HCl showed the highest supersaturation in comparison with atmospheric mixing ratios, which did not exceed 80 pptv in this region during austral summer [Piel, 2004]. The fact that Cl⁻ concentrations in firm layers older than one year were preserved suggests that the main part of Cl⁻ was located inside the ice crystals. The Cl/Na ratios measured in our samples support the existence of solid seawater condensation nuclei inside ice crystals as found by Kumai [1976] but this point remains controversial [Cullen and Baker, 2001]. MSA showed the lowest supersaturation, provided that gaseous MSA of around \(5 \times 10^{-3}\) pptv observed at South Pole [Mauldin et al., 2001] are typical in continental Antarctica during austral summer. However, gaseous atmospheric MSA concentrations and Henry’s law constant for MSA appear highly uncertain and no temperature dependent measurements of \(H_{\text{MSA}}\) are available, making a conclusive discussion difficult.

[17] Finally, we have to assess to what extent our simplifications may be responsible for the obvious discrepancies between the model approach and observations. For MSA⁻, temperature dependent activity coefficients and the effect of mixed electrolytes on \(\gamma\) ± is not available for the ionic composition to be considered here. Measurements performed by Cerquetti et al. [1968] indicate that \(\gamma\) ±(HCl) at 243 K should be higher by about a factor of 1.6 compared with the value at 298 K. The impact of mixed electrolytes is complex to assess, but even changing the corresponding activity coefficients by a factor of 10 would only alter \(p_{HA}\)
by less than an order of magnitude. Even in this case a nearly quantitative postdepositional loss of HA should be expected. Accordingly, these shortcomings can hardly account for the inconsistency between observations and model approach.

[18] Evidently, our approximation that all ionic impurities are quantitatively accumulated within the QBL is the most critical point. As shown in the extensive work of Gross [1968] the water/ice phase distribution coefficients $\Gamma$ of ionic impurities are on the order of $10^{-3}$ to $10^{-5}$ hence comparable to the volume ratio QBL/ice. Consequently, only a miniscule part of the ionic impurities may be located in a QBL. Recently $\Gamma$(HNO$_3$) has been determined to be $3 \times 10^{-6}$ to $1.6 \times 10^{-5}$ in the temperature range between 265 K and 238 K, respectively [Thibert and Domine`1998]. According to Thibert and Domine` [1997, 1998] about 60 $\mu$g/g HCl and 1.8 $\mu$g/g HNO$_3$ can potentially be dissolved within the ice lattice, much more than typically found in our samples. In addition, recent scanning electron microscopy studies revealed that most of the chloride in polar ice seems to be located within the lattice [Barnes et al., 2003]. Extrapolating the partial pressure equations given by Thibert and Domine` [1997, 1998] to our conditions ($T=243$ K, $[\text{HCl}]_{\text{ice}}=0.79$ nmol g$^{-1}$, $[\text{HNO}_3]_{\text{ice}}=0.79$ nmol g$^{-1}$) result in $p_{\text{HCl}}=2 \times 10^{-10}$ Pa (i.e., about $3 \times 10^{-3}$ pptv) and $p_{\text{HNO}_3}=1.6 \times 10^{-6}$ Pa (i.e., about 22 pptv). Consequently during summer the firm should be highly undersaturated with HCl but roughly in equilibrium for HNO$_3$ regarding typical atmospheric concentrations (see Table 4). Nevertheless, the QBL approach is consistent with recent encouraging progress achieved in modeling the re-emission of volatile acids from firn layers, comparable to recent encouraging progress achieved in modeling the air-snow interaction of HCHO and H$_2$O$_2$ [McConnell et al., 1998; Hutterli et al., 2002]. We emphasize the need of laboratory investigations to substantiate the presence of QBLs and to determine electrolyte concentrations in those phases, as well as field measurements to assess firm air concentrations of MSA, HNO$_3$ and HCl. Such measurements would help to understand the microphysical reason of postdepositional losses and shed some light on the physicochemical processes acting during snow metamorphism in the upper firm layers.

[20] Our investigations on postdepositional losses of MSA$^-$, Cl$^-$, and NO$_3^-$, based on the analysis of 13 snow pits and 4 medium depth firm cores provided representative values on total loss and loss rates for the region of Amundsenisen. In contrast to MSA$^-$, the concentration of the ions Cl$^-$ and NO$_3^-$ exhibited only a marginal dependence on snow accumulation rate in the area of investigation. Moreover, only postdepositional losses of MSA$^-$ strongly depend on snow accumulation rate which is obviously the controlling factor for the observed relation between MSA$^-$ concentrations stored in firm and accumulation rate. Given that even during Holocene the accumulation rate may vary by a factor of two [Oerter et al., 2000], we recommend a correction of MSA$^-$ profiles in firm and ice cores retrieved at this site according to expression (1). We emphasize that the proposed correction is only valid for sites with snow accumulation rates between 50 kg m$^{-2}$ yr$^{-1}$ and 100 kg m$^{-2}$ yr$^{-1}$ and mean annual temperatures around $-46$°C. At accumulation rates above 100 kg m$^{-2}$ yr$^{-1}$ postdepositional losses become insignificant for all species considered here. In addition loss processes by re-emission of volatile acids should be marginal during glacial periods where high dust entries neutralize strong acids as supported by Röthlisberger et al. [2000, 2003].

5. Conclusions

Our investigations on postdepositional losses of MSA$^-$, Cl$^-$, and NO$_3^-$, based on the analysis of 13 snow

References


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